

5 **Functional Classification of Swine Manure Management Systems Based on**
6 **Effluent and Gas Emission Characteristics**

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ABSTRACT

Gaseous emissions from swine manure storage systems represent a concern to air quality due to the potential impacts of hydrogen sulfide, ammonia, methane, and volatile organic compounds on environmental quality, human health, and wellbeing. The lack of knowledge concerning functional aspects of swine manure management systems has been a major obstacle in the development and optimization of emission abatement technologies for these point sources. In this study, a classification system based on gas emission characteristics and effluent concentrations of total phosphorus (P) and total sulfur (S) was devised and tested on 29 swine manure management systems in Iowa, Oklahoma, and North Carolina in an effort to elucidate functional characteristics of these systems. Four swine manure management system classes were identified that differed in effluent concentrations of P and S, methane (CH₄) emission rate, odor intensity, and air concentration of volatile organic compounds (VOCs). Odor intensity and the concentration of VOCs in air emitted from swine manure management systems were strongly correlated ($r^2 = 0.88$). The concentration of VOC in air samples was highest with outdoor swine manure management systems that received a high input of volatile solids (Type 2). These systems were also shown to have the highest odor intensity levels. The emission rate for VOCs and the odor intensity associated with swine manure management systems were inversely correlated with CH₄ and ammonia (NH₃) emission rates. The emission rate of CH₄, NH₃, and VOCs were found to be dependent upon manure loading rate and were indirectly influenced by animal numbers.

Key Words: Odor, Swine Production, Manure Management, Volatile Organic Compounds, Concentrated Animal Feeding Operations.

Abbreviations: FID, Flame ionization detector; GC, Gas chromatography; ICP-AES, Inductively-coupled plasma-atomic emission spectrometry; TD, Thermal desorption; VOC, Volatile Organic Compound.

INTRODUCTION

In the United States, approximately 157,000 swine production facilities produce 103,000,000 hogs yr⁻¹ that are marketed in the U.S. and globally (ASAE, 1988; Harkin, 1997). Annually, these production facilities produce more than 116,652,300 tons yr⁻¹ of manure that is often stored for periods up to 13 months before land application (ASAE, 1988; Harkin, 1997). Air quality studies have indicated that emissions released from stored swine manure have the potential to decay local, regional, and global air quality through the discharge of ammonia (NH₃) (Harper and Sharpe, 1997; Asman, 1995), nitrous oxide (N₂O) (Sharpe and Harper, 1998), methane (CH₄) (Safley et al., 1992; Sharpe and Harper, 1997), hydrogen sulfide (H₂S) (Jacobson et al., 1997a), particulate matter (VanWicklen, 1997), and volatile organic compounds (VOCs) (Zahn et al., 1997). Much research has focused on the development of strategies to reduce or eliminate emissions and odors from stored animal manure. However, a major part of this research has not been applied by the swine industry due to economic restrictions or due to sporadic or ineffective performance of emission abatement approaches (Miner, 1982; Miner, 1995; Miner, 1999). Performance evaluations of emission abatement strategies often cite poorly understood microbiological processes or other poorly defined intrinsic properties of swine manure management systems as the reason for ineffective performance of a particular emission abatement method (Miner, 1995). However, the exact cause for many of these failures has remained speculative due to the lack knowledge concerning functional aspects of animal manure management systems.

The purpose of this research was to develop a method to functionally classify swine manure management systems based on effluent chemical properties and emission rates of CH₄, NH₃, H₂S, and VOC. A reliable method to functionally classify manure management systems would serve the agricultural industry as a management tool in evaluating best management practices for swine manure storage systems and would serve regulators as a rapid method to identify production sites that represent a potential air quality or nuisance concern.

MATERIALS AND METHODS

Physical and Chemical Characterization of Stored Manure

Effluent samples (200 ml each) and pH were taken at six locations at the center and around the perimeter of the manure management system at a minimum distance of 2.5 meters from the edge of the storage impoundment and at a depth of 2 cm according to the method of DiSpirito et al., (1995). Measurements of pH were taken with a portable pH/temperature meter (Model #59002-00, Cole Parmer, Vernon Hills, IL). Total carbon (C), nitrogen (N), and hydrogen (H) were determined on oven (100° C) dried effluent samples using a Model 2100 Perkin Elmer CHN analyzer. Percent values were converted to g L⁻¹ values based on solids content determined by gravimetric methods. Volatile solids concentration was determined by the difference in weight of oven-dried (100° C) and ashed (550° C) samples. Analysis of main-group elements and transition metal cations was performed on microwave digested (method SW 846-3015, CEM Corp., 1996) effluent samples according to EPA method SW 846-3015 (CEM Corp., 1996). Quantitative analysis of digested samples was performed using a Thermo Jarrel Ash Model ICAP 61E Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) and elemental concentration is reported as the mean \pm the standard error. Other physical and chemical parameters evaluated in this study included bacterial chlorophyll *a* and *b* concentration. Bacteriochlorophyll *a* and *b* was determined as previously described by Siefert et al. (1978) and DiSpirito et al. (1995). The bacteriochlorophyll *a* concentration was calculated spectrophotometrically using a molar absorptivity coefficient of $\epsilon_{777} = 75 \text{ cm}^{-1} \text{ mM}^{-1}$. Lagoons with bacteriochlorophyll *a* concentrations above 40 nmol/ml are subsequently referred to as “photosynthetic lagoons”.

Description of Swine Manure Storage Facilities, Placement of Air Monitoring Equipment, and Statistical Analyses

Loading criteria and individual site descriptions for 29 swine manure management systems located in Iowa (n = 24), Oklahoma (n = 2), and North Carolina (n = 3) that were sampled during the months of August and September 1997 are described in Table 1. Individual manure management systems were separated into four main categories (Type 1, Type 2, Type 3, and Type 4) based on the concentration of total P and total S present in effluent samples. Average

physical and chemical properties, as well as management attributes for these systems are summarized in Table 1. Meteorological conditions (wind speed, relative humidity, irradiance, solution temperature at a 10 cm depth, and air temperature) were monitored continuously and the sample mean was recorded in 0.5 minute intervals at the point of air sample collection by an integrated weather station (Sauer and Hatfield, 1994) that was positioned at the center of the outdoor manure storage systems. Height of the sensors was established by trajectory simulation models described in the micrometeorological flux methods section (theoretical profile shape) and was identical to the air sampling height used for micrometeorological flux measurements. Micrometeorological data was not collected for studies that employed dynamic flux chamber methods for determination of CH₄ flux rates.

Statistical evaluation of data and experimental designs were performed with JMP version 3 statistical discovery software (SAS Institute, Inc., Cary, NC).

Capture and Analysis of Air Pollutants from Swine Manure Management Systems

Volatile organic compounds (VOC) were captured on a multibed adsorbent tube containing a combination of Tenax TA and Carboxen-569 (Supelco, Bellefonte, PA), according to the low-volume sampling method developed by Zahn et al. (1997). For air sampling of VOC, flow rate through individual thermal desorption tubes was precisely regulated at 1.0 L min⁻¹ throughout the 30 min sampling period, using thermal mass flow controllers (Series 810, Sierra Instruments, Inc., Monterey, CA) that were connected to a common, high-vacuum manifold. Desorption tubes were analyzed by gas chromatography using a flame ionization or mass selective detector as previously described by Zahn et al. (1997).

Ammonia (NH₃) was collected from air using two glass impingers (210 ml internal volume) arranged in series, each containing 25 grams of 2 mm glass balls. Air samples were drawn by vacuum through a submerged fritted glass diffusion tube into 60 ml of 0.2M boric acid using a Buck IH sampling pump operated at 1.0 L min⁻¹. The boric acid solution was replaced in 30 to 120 minute intervals depending on proximity of the sampler to the emission source. Ammonium concentration was determined by the salicylate-nitroprusside technique according to U.S. EPA method 351.2 (U.S. EPA, 1979). Solutions of ammonium chloride in 0.2M boric acid were utilized as reference standards to determine ammonium ion concentration. Hydrogen sulfide

(H₂S) and CH₄ were collected in 1.0 L Tedlar gas sampling bags and evaluated in the laboratory by previously described gas chromatographic methods using either a 0.32 mm x 30 m SPB-1 sulfur fused silica column with flame photometric detection (Bulletin 876, Supelco, Inc., Bellefonte, PA) or a 1/8" x 8' HayeSep-Q packed column with thermal conductivity detection (Chan et al., 1998), respectively. Air samples for H₂S and CH₄ analysis were drawn by vacuum into 1.0 L Tedlar gas sampling bags using a model 1062 grab sampler (Supelco, Bellefonte, PA) operated at 25 mL min⁻¹. Teflon surfaces were equilibrated with analytes (H₂S and CH₄) present in the air sample by performing four fill-purge cycles before collection of the final air sample. Lead acetate strips (Model #701, VICI Metronics Inc., Santa Clara, CA) were utilized at the point of air sample collection (by Tedlar bag methods) to confirm gas chromatographic results for the quantification of H₂S. The latter methods indicated that H₂S losses due to reaction or condensation were less than 4% if samples were analyzed within 6 hours of collection. The concentration of CH₄ in air was also determined in real-time at two of the 29 swine manure management systems noted in Fig. 1 using a tunable-diode laser system operated in the infrared region at 2968.4034 cm⁻¹, as previously described by Simpson et al., (1995). Concentration measurements of CH₄ that were determined using the tunable-diode laser were converted to flux using the theoretical profile shape micrometeorological method. All other CH₄ flux measurements performed in this study used CH₄ concentration measurements that were determined by the gas chromatographic method. A combination of the air sampling methods described above were used to determine recovery efficiency and to validate the H₂S and CH₄ sampling techniques.

Evaluation of the Odor Intensity Associated with Swine Manure Management Systems

Odor intensity was measured by the method of direct scaling in reference to an odor standard of defined intensity using three to four trained panelists (Cain et al., 1998; Degel and Koster, 1998; Liden et al., 1998; Livermore and Laing, 1998). Direct scaling was based on estimation of the intensity of olfactory sensations associated with an odor source by assigning numerical values to sensory stimuli. Sensory responses were normalized against the artificial swine odor reference standard "Z-2" (Zahn and DiSpirito, 1999), that consisted of: 0.05 mM dimethyl disulfide, 8 mM acetic acid, 3.5 mM propionic acid, 0.5 mM isobutyric acid, 0.4 mM 2-butanol, 1.4 mM butyric

acid, 0.2 mM isovaleric acid, 0.5 mM valeric acid, 0.1 mM isocaproic acid, 0.2 mM caproic acid, 0.2 mM heptanoic acid, 0.1 mM indole, 0.15 mM 3-methyl indole, 0.2 mM 4-methyl phenol, 0.12 mM 4-ethyl phenol, 0.15 mM phenol, 0.1 mM benzyl alcohol, 0.15 mM 2-amino acetophenone, 0.1 mM butylated hydroxytoluene (added as a preservative), and 8 mM ammonium acetate. Chemical composition of the artificial swine odor Z-2 was optimized in a laboratory dynamic flux chamber to mimic emission parameters for VOCs emitted from a manure sample collected from a high-odor, Type 1 swine manure management system (Zahn et al., 2000b). Pure compounds were dissolved in warm (45° C) water while stirring and the solution pH was frequently adjusted to pH 7.0 with 2 M potassium hydroxide. Approximately 15 mL of the solution was transferred to an amber serum vial (30 ml nominal volume), was capped with a silicone/Teflon septum, and then degassed under repeated cycles of vacuum and argon to create an anaerobic headspace. Samples were stored in the dark at ambient temperatures until they were used. Panelists were provided the synthetic swine odor solution Z-2 in an uncapped 30 ml serum vial, a solution of 2 mM n-butanol in a 30 ml serum vial, and a site odor evaluation worksheet, previously described by Zahn (1997). Panelists then evaluated the n-butanol solution that was considered neutral (grade 3/10), and the Z-2 solution that was considered unpleasant (grade 6.5/10), at a neutral distance (>1000 m) from the manure management system. Panelists were then positioned in the emission plume from the manure management system (1.5 m from the emitting source at a height of 1.5 m) and asked to compare the odor intensity to the reference standards. Numerical evaluations of the swine manure management systems ranged from neutral (3) to unbearable (10), and are reported as the sample mean. Air samples for VOC analysis were collected at the receptor (1.5 m from the emitting source at a height of 1.5 m) throughout the odor evaluation period.

Measurement of CH₄ Flux, VOC Concentration, and Odor Intensity from 29 Swine Manure Management Systems

An initial screening study was completed at 29 swine manure management systems to measure the flux rate of CH₄, odor intensity, concentration of VOCs in air at the point of the odor intensity measurements, and analytes in the effluent fraction. The flux rate of CH₄, for this initial screening study, was measured at 29 manure management systems (lagoons, earthen basins,

cement-lined basins, steel-lined tanks, and confinement pits) using a flux chamber described by DiSpirito and Zahn (1998). The dynamic flux chamber method was found to be most suitable for screening large sample numbers due to the minimum operation requirements, portability, and reliability for measurement of non-reactive gases such as CH₄ (Chan et al., 1998). The dynamic flux chamber was positioned near the center of the swine manure management system, with the exception of deep and shallow pit systems, which were sampled at the pump-out positions near the wall of the pit. Chamber operational parameters were modified from semi-static to dynamic mode by installation of a sweep gas manifold. Compressed air (containing 1.1 parts per million by volume or 0.77 mg m⁻³ CH₄) sweep gas was provided to the enclosure at a flow rate of 2.0 L min⁻¹ in a demand mode. Air pressure within the chamber was maintained at barometric pressure through the use of a silicone oil (impinger) purge valve, positioned on the gas supply manifold. The static pressure differential was maintained at 0 ± 1.5 kPa throughout the collection period with the use of a mercury manometer. Gases were removed from the chamber through 0.635 cm ID Teflon tubing that was attached to a vacuum pump through an inline mass flow controller set at 2.0 L min⁻¹, following a 1 hr chamber equilibration period. Six individual air samples (~750 ml each) were collected over a 3-hour sampling period. Samples were analyzed for CH₄ concentration by gas chromatography within 6 hours of sample collection. The concentration of CH₄ in air samples was converted to trace gas flux density (f) through the equation:

$$(1) \quad f = (s/a) (C_o - C_i) \text{ where:}$$

s = sweep flow rate (2.025 L min⁻¹), A = chamber basal area (2500 cm²), C_o = concentration of methane in the exit air (mg m⁻³), and C_i = concentration of CH₄ in the sweep gas (0.77 mg m⁻³).

In addition to the collection of samples for CH₄ flux measurements, odor intensity and VOC concentration in air were taken at the receptor (1.5 m from the emitting source at a height of 1.5 m). Samples were collected at 1.0 L min⁻¹ during the 30 min olfactory evaluation period.

Detailed Studies of Gas Flux Rates from Four Swine Manure Management Systems

The flux rate of CH₄, H₂S, NH₃, and VOCs was measured continuously at four swine manure management systems, throughout a 24 hour period using the theoretical profile shape micrometeorological flux measurement method. The four sites chosen for this comprehensive study represented each of the four classes of swine manure management systems defined in Table

1. The theoretical profile shape method was chosen instead of chamber methods, since the latter methods adversely affected VOC emission profiles. Higher flux rates of disulfide compounds (dimethyl disulfide and dimethyl trisulfide) and lower flux rates of sulfide compounds (methyl mercaptan) were consistently observed with flux chamber methods when compared to micrometeorological methods. This observation indicated that the chamber surfaces were potentially the site of oxidation reactions for reactive gases (H_2S , NH_3 , and VOCs). These results are consistent with previous studies that show significant reduction in the concentration of VOCs collected from air if samples were drawn through glass or polymeric tubing (Zahn et al., 1997).

The flux of NH_3 , H_2S , CH_4 , and VOCs from the lagoon were measured using the theoretical profile shape method described by Wilson and coworkers (1982). The emission rate of gases from a circular source plot was calculated with the following equation:

$$(2) \quad \bar{F}_z(0) = \frac{(uc)_{measured}}{\Phi}$$

Where $\bar{F}_z(0)$ is the vertical flux rate in $\mu\text{g cm}^{-2} \text{ s}^{-1}$, Φ is the non-dimensional normalized horizontal flux predicted by the trajectory simulation model and $(uc)^{measured}$ is the product of the measured average wind velocity and air concentration of analyte in m s^{-1} and $\mu\text{g m}^{-3}$, respectively (Majewski et al., 1989; Majewski, 1990). Flux measurements were completed at the center of swine waste management systems with a circular shape. System classification based on the concentration ratio of phosphorus to sulfur (Table 1) and the requirement for circular manure management systems served as the major criteria for selecting the four swine waste management systems that were sampled for follow-up studies.

The surface roughness was determined before the sampling period began by performing mean wind velocity profile measurements at 0.2, 0.5, 1.0, 2.0, and 3.0 m for a period of 1 hour at the center of the swine manure management system with cup anemometers (model 03101-5, R.M Young Co., Traverse City, MI). The mean value for roughness length at the surface of outdoor swine manure management systems, during periods of neutral atmospheric stability (mid-morning), was 0.10 ± 0.02 cm (mean \pm std. error). The following measurement parameters were used to establish the sampling height: Type 1 = total mechanically-ventilated exhaust flow rate = $110,000 \text{ m}^3 \text{ hr}^{-1}$, sampling position at the fan orifices (4 total); Type 2 = 39 m diameter basin,

z=ZINST(0.1 cm roughness length, 1950 cm radius = 70 cm sampling height); Type 3 = 92 m diameter lagoon, z=ZINST(0.1 cm roughness length, 4600 cm radius = 189 cm sampling height); Type 4 = a primary 100 m diameter photosynthetic lagoon, z=ZINST(0.1 cm roughness length, 5000 cm radius = 191 cm sampling height). Error in measurement height that was associated with temporal changes in roughness length for the lagoon surface was estimated to cause a maximum error of 8% in the height parameter for emission measurements.

Flux measurements using the theoretical profile shape method were based on the concentration of airborne analytes present at a measurement height (z) and meteorological data, collected at the same point (Majewski, 1990). Measurement height (z) was calculated by trajectory simulation models and was based on system surface area and roughness length (Wilson et al., 1982). In addition to the air samples that were collected over the emitting source, 2-5 air samples were collected at the beginning of each sampling period, upwind from each manure storage system, to assess background air concentrations of target analytes and to confirm the source of these emissions. Background analyte concentrations were assumed to remain constant throughout the sampling period and were subtracted from analyte concentrations that were observed above each emitting source. Background concentrations for analytes at each of the four sites sampled in follow-up studies were: Type 1: 6.0 parts per billion by volume (ppbv) ($8.5 \mu\text{g m}^{-3}$) H_2S , 15.0 ppbv ($11.1 \mu\text{g m}^{-3}$) NH_3 , and 1.3 parts per million by volume (ppmv) (0.91 mg m^{-3}) CH_4 . Type 2: 15 ppbv ($21.3 \mu\text{g m}^{-3}$) H_2S , 11.0 ppbv ($8.1 \mu\text{g m}^{-3}$) NH_3 , and 1.3 ppmv (0.91 mg m^{-3}) CH_4 . Type 3: 12 ppbv ($17.1 \mu\text{g m}^{-3}$) H_2S , 7.0 ppbv ($5.2 \mu\text{g m}^{-3}$) NH_3 , and 1.2 ppmv (0.84 mg m^{-3}) CH_4 . Type 4: 9.0 ppbv ($12.8 \mu\text{g m}^{-3}$) H_2S , 8.0 ppbv ($5.9 \mu\text{g m}^{-3}$) NH_3 , and 1.3 ppmv (0.91 mg m^{-3}) CH_4 . The concentration of VOCs in background air samples was below the detection limit of 0.2 ppb for all samples that were analyzed.

Flux rate measurements for the mechanically-ventilated deep-pit swine manure management system (animal confinements) was performed by continuously monitoring exhaust flow rate during the sample collection period at two pit fan and two ventilation fan orifices using a 3-D sonic anemometer (Campbell Scientific, Logan, UT). Air samples were collected near the lower sensor arm on the anemometer in the exhaust stream.

RESULTS AND DISCUSSION

Initial Evidence that Methane Emission Rate is Dependent Upon Manure Management System Environment

Studies were conducted on two types of manure management systems located on a feeder-to-finish swine production facility in central Iowa in August 1997 to assess differences in CH₄ emission rate that could be attributed to differences in manure management system environment. Swine waste material entering the manure management system environments originated from animals of the same breeding population that were fed identical diets, were of similar weight, and were managed under similar management routines (feeding schedules and rates). Volatile solids loading rate, however, differed between the two systems by over 300-fold (37 *versus* 0.12 kg volatile solids day⁻¹ m⁻³). For the basin system (37 kg volatile solids day⁻¹ m⁻³), manure was emptied daily from the confinement into an outdoor concrete holding tank and for the lagoon system (0.12 kg volatile solids day⁻¹ m⁻³), manure was flushed into the earthen holding basin by an intermittent loop flush system. Methane flux measurements were performed on three separate occasions in August 1997 with a tunable-diode laser over the center of the manure management systems using the theoretical-profile-shape method for measuring evaporative fluxes (Fig. 1). While similar CH₄ flux values were observed for systems over the three separate sampling periods, only a single comparison is reported, since this sampling period demonstrated the greatest similarity between sites for environmental conditions known to influence CH₄ flux. Measured environmental conditions over the 68 hour sampling period included wind speed (2.2±0.14 *versus* 2.4±0.12 m s⁻¹ [mean and standard error mean]), irradiance (298±35 *versus* 305±30 W cm⁻²), relative humidity (RH) (85±2 *versus* 78±2 % RH), air temperature (18.6±0.4 *versus* 22.6±0.5°C) and solution temperature at a 10 cm depth (27±0.2 *versus* 23±0.3°C) for the lagoon and basin, respectively. Results from CH₄ micrometeorological flux measurements indicated that there were statistically-significant differences in both the flux rate (0.35±0.02 *versus* 0.13±0.01 µg CH₄ cm⁻² s⁻¹ [mean and standard error mean]) and emission rate (14.7 *versus* 0.5 g CH₄ system⁻¹ s⁻¹) for the lagoon and basin, respectively (Fig. 1). Current literature values for CH₄ emissions from stored swine manure have been reported over a range of nearly two orders of magnitude (Harper and Sharpe, 1997). Harper and Sharpe (1997) proposed that the discrepancies between emission values might be explained by differences in measurement methods or due to atypical flux event periods. In addition to these explanations, results described

1 in these experiments indicate that manure management environment, and specifically loading
2 rate, may significantly influence the flux rate of CH₄. While these observations are not novel in
3 the context of laboratory anaerobic digestion processes (Oleszkiewicz and Sharma, 1990; Hill
4 and Bolte, 1989), they do represent the first report of such a phenomena occurring under
5 production scale conditions in an animal manure management system. The proceeding
6 experiments were focused on defining relationships between effluent chemical properties of
7 various swine manure management systems and observed emission characteristics in order to
8 further define the relationship between system loading rate and emission rate of CH₄, NH₃, H₂S,
9 and VOCs.

11 **Classification of 29 Swine Manure Management Systems Based on Solution-** 12 **Phase Chemistry and Methane Emission Rate**

13 The concentration range for elements found in the swine manure storage systems sampled in
14 this study were found to be similar to those previously reported by Giusquiani et al (1998),
15 Japenga and Harmsen (1990), and Zahn et al (1997) (Table 1). There was a weak positive
16 correlation observed between volatile solids loading rate and concentration of elements for each
17 of the samples evaluated (Table 1). Individual correlations between element concentration and
18 volatile solids loading rate indicated that volatile solids loading rate could account for 48 to 76%
19 of the variability observed with effluent concentration of elements. This inadequacy of volatile
20 solids loading rate to account for differences in effluent elemental composition for various swine
21 manure management systems, in addition to the low-throughput of volatile solids measurements,
22 indicated that the solution concentration of elements may provide a more appropriate means to
23 classify swine manure management systems.

24 In the search for useful effluent chemical classification criteria, 45 pairwise comparisons
25 were made between the concentrations of elements present in the 29 site samples. The
26 nonparametric measure of association for each pairwise comparison is shown in Table 2. In
27 general, a lower level of correlation was observed for pairwise comparisons made between
28 elements showing opposite partitioning behavior (Table 2). For example, transition metal ions
29 have been shown to partition strongly into the sludge or particulate fraction of the manure, while
30 sodium (Na), potassium (K), and to a lesser extent, phosphorus (P), magnesium (Mg), and sulfur

(S), demonstrate neutral or preferential partitioning behavior into the supernatant fraction of the manure (Giusquiani et al., 1998; Zahn et al., 1997). Therefore, the concentration of transition metal ions in samples is highly dependent upon the concentration of suspended solids, while Na and K are nearly independent of the concentration of suspended solids. High correlation coefficients were observed for pairwise comparisons between several transition metals, for several transition metals and a small number of main group elements, and finally, for P and S concentrations in the 29 site samples. However, only one pairwise comparison (P and S) demonstrated clear functional clustering of manure management systems based on system CH₄ emission rate, air concentration of VOCs, or odor intensity (Fig. 2, Table 2).

The 29 swine manure management systems were observed to cluster into four distinct system subtypes (Type 1, Type 2, Type 3, and Type 4) based on the concentration of S and P in the effluent fraction (Fig. 2, Table 1). No statistical differences were observed for CH₄ emission rates between Type 1 and 2 systems, nor between Type 3 and 4 systems. However, CH₄ emission rates for all other comparisons were statistically different (Fig. 2B). The mean odor intensity values for sampling sites showed a clustering behavior that was similar to the clustering of data points based on effluent P and S concentrations or system CH₄ emission rate. However, odor intensity showed nearly an inverse relationship to CH₄ emission rate, with the highest odor intensities occurring with manure management systems having the lowest CH₄ emission rates (Type 1 and 2 systems).

Odor intensities and VOC concentrations in Type 2 systems were consistently higher than measurements performed on Type 1 systems. This result was not entirely consistent with effluent P and S concentrations or with system CH₄ emission rates, which predicted Type 1 systems to have the highest odor intensities and air concentrations of VOCs. Gas transfer coefficients for CH₄ and VOCs are known to differ by several hundred-fold (MacIntyre et al., 1995). In addition to large differences in gas transfer coefficients for CH₄ and VOCs, surface exchange rate for some VOCs is known to be influenced by effluent chemical events that include ionization (pH), hydrogen bonding, and surface slicks (MacIntyre et al., 1995). For these reasons, CH₄ is not an appropriate criterion for predicting VOC volatilization potential between swine manure management systems. Wind, temperature, and irradiance are known to be major factors in the emission rate of sparingly soluble gases (VOCs) from liquid or semi-solid surfaces (MacIntyre et

1 al., 1995; Zahn et al., 1997). Based on the VOC transfer coefficient calculations from MacIntyre
2 et al. (1995), the difference due to wind and temperature exposures between outdoor and indoor
3 manure management systems can account for between 51% to 93% of the observed differences in
4 VOC emissions. This analysis provides evidence that exposure factors can account for
5 differences observed in VOC flux rates, VOC air concentrations, and odor intensity between
6 Type 1 and 2 systems.

7 Swine manure management systems are often designed to release gases produced in
8 anaerobic decomposition processes into the atmosphere. Within these systems, a complex
9 consortium of microorganisms (anaerobic food chain) decompose complex biological waste
10 material to end products including CH₄, H₂S, CO₂, and NH₃ (Gottschalk, 1988; Lana et al., 1998;
11 Mackie et al., 1998; Fenchel and Finlay, 1994). The anaerobic food chain is often functionally
12 separated into microorganisms catalyzing acid-producing reactions from complex organic
13 substrates and *Archaea*, that catalyze CH₄-producing reactions from products formed in the
14 breakdown of complex organic substrates (Deppenmeier et al., 1996; Fenchel and Finlay, 1994).
15 The emission rate of CH₄ and partially decomposed microbial substrates (volatile fatty acids) has
16 been previously employed as an indicator to assess functional coupling between processes in the
17 anaerobic food chain in anaerobic digesters (Hill and Bolte, 1989). Overloaded anaerobic
18 digestion processes have been correlated with high emission rates of VOCs and low emission
19 rates of CH₄, while optimum loading rates promote high bioconversion efficiencies of complex
20 organic matter into CH₄ (Hill and Bolte, 1989). Data in Figure 2 and Table 1 provide evidence
21 that the biological processing events occurring in high-load systems (Type 1 and Type 2) may
22 result from the functional decoupling of the anaerobic food chain. This observation is further
23 supported by the fact that these same systems show an accumulation of organic (particulate C, H,
24 N) material (Table 1) and high air concentrations of VOCs (Fig. 3; Table 3). In contrast, the high
25 emission rates for CH₄ and low liquid-phase organic content (particulate C, H, N) associated with
26 Type 3 and 4 systems (Table 1) indicates that the environment in these systems provides for
27 relatively more efficient bioconversion of complex organic substrates into CH₄.

28 Data reported in this study were collected in three geographical regions of the U.S. over a
29 six week period in the late summer (August and September, 1997). This experimental design
30 was chosen based on previous reports that bacterial photosynthetic and SO₄ reduction activities

1 in swine manure management systems located in northern U.S. climates reach a near steady-state
2 condition during this time period (Do et al., 1998; Do et al., 1999; Jacobson et al., 1997b). A
3 second objective of this design was to identify differences in emission or effluent properties of
4 swine manure management systems that could be attributed to geographical location (Iowa, n =
5 24; Oklahoma, n = 2; and North Carolina, n = 3). However, no significant differences were
6 observed in any of the parameters measured in this study when “like” manure management
7 systems (i.e., photosynthetic lagoons *versus* photosynthetic lagoons) were compared on the basis
8 of geographic location. While the certainty of this finding is diminished by the low sample
9 number, it was not entirely surprising that effects of geographic location played a minor role in
10 the emission characteristics of (steady-state) manure management systems when contrasted to the
11 effects due to loading rate. While the effects of geographic location on emission parameters
12 appeared to be insignificant, geographic location was found to influence the rate at which the
13 apparent steady-state condition was achieved. Based on the population dynamics of purple non-
14 sulfur photosynthetic populations, it has been noted that that the apparent steady-state condition
15 occurs at least 1.2 months earlier in North Carolina lagoons when compared to comparable
16 lagoon systems in Iowa (Do et al., 1998). The seasonal transition in P and S concentrations for
17 photosynthetic lagoons in Iowa progress from “basin-like” characteristics in early spring (100 mg
18 L⁻¹ P and 30 mg L⁻¹ S) to intermediate concentrations (“lagoon-like”) in late spring (60 mg L⁻¹ P
19 and 16 mg L⁻¹ S), to low concentrations during the photosynthetic bloom event in late June (1
20 mg L⁻¹ P and 8 mg L⁻¹ S) (Do et al., 1998). Maximum methane flux during these transition
21 events was observed to occur shortly (2-9 days) before the photosynthetic bloom (Do et al.,
22 1998). These studies indicate that the P and S concentrations may provide valuable swine
23 manure management classification information regardless of the season or geographical location.

24 25 **Relationships between Emission Chemistry and Odor Intensity**

26 Several recent investigations have attempted to define relationships between chemical
27 concentration of specific gases and odor concentration or intensity (Hobbs et al. 1995, Jacobson
28 et al. 1997a, Jacobson et al. 1997b, Obrock-Hegel 1997, Pain et al. 1990). Obrock-Hegel (1997),
29 found that nutritional manipulation of amino acid intake reduced NH₃, cresols, and indoles
30 measured in air samples from production environments. However, no reduction in odor

1 concentration was observed between control and treatment samples. Schulte et al. (1985) and
2 Hobbs et al. (1995), linked high levels of ammonia (NH_3) to odor. Unfortunately, the latter
3 authors noted that the relationship between NH_3 and odor could not be universally applied to all
4 farms, especially when they differed in the type of manure management system utilized. The use
5 of hydrogen sulfide (H_2S) as a surrogate of livestock manure odor has also proven to be a
6 formidable challenge. Jacobson et al., (1997a) evaluated odor and H_2S concentration in air from
7 approximately 60 different pig, dairy, beef, and poultry manure storage units on farms in
8 Minnesota. Low correlation was observed between H_2S and odor concentration for manure
9 storages based on a species comparison and for production systems grouped according to manure
10 management system type (pit, basin, and lagoon). The study further suggested the possibility that
11 chemical odorants other than H_2S (i.e., VOCs) were responsible for swine odor. In support of
12 this conclusion, Powers et al., (1999) recently demonstrated that effluent concentrations of
13 several VOCs, present in anaerobic digester effluent were correlated with odor intensity.
14 However, effluent concentration of VOC did not predict odor intensities well enough to suggest
15 that human panels should be eliminated. Data quality in this study was likely influenced by the
16 fact that correlations were not performed in a similar matrix (air *versus* liquid). Previous studies
17 have established that effluent measurements often provide an inaccurate representation of
18 malodor potential and therefore, represent an inappropriate comparison (Zahn et al., 1997).

19 To test the potential relationship between airborne VOCs and swine manure odor, odor
20 intensity and air concentration of VOCs were determined simultaneously at the 29 swine
21 production facilities. Figure 2C shows the relationship between average odor intensity, assessed
22 through direct scaling techniques using a defined odor intensity, and the total air concentration of
23 VOCs present at the receptor. The relationship between mean odor intensity and air
24 concentration of VOCs was observed to obey Michaelis-Menten kinetics, with a Michaelis
25 constant (K_m) of $95 \mu\text{g m}^{-3}$ VOCs and receptor saturation occurring at $1250 \mu\text{g m}^{-3}$ VOCs (Fig.
26 2). The saturation properties showed typical second-order kinetics and were characteristic of a
27 receptor-ligand process. A qualitative analysis of VOCs present at sites representing the four
28 classes of swine manure management systems is shown Figure 3 and Table 3. The gas
29 chromatography-flame ionization detector (GC-FID) chromatograms from deep pits or basins
30 produced high odor intensities and relatively intense signal responses but were chemically-

1 simplistic in nature when compared to chromatograms from lagoons (Fig. 3; Table 3). These
2 results provide evidence that chemical concentration rather than diversity is the largest
3 determinate in the odor intensity response associated with swine manure odor. This observation
4 is important since the ability to define odorant synergisms and antagonisms has been suggested to
5 be the most significant obstacle in applying chemical methods in odor measurement (Mackie et
6 al., 1998). Data presented in Figure 2C provide evidence that the total air concentration of non-
7 methane VOCs predict the odor intensity associated with swine manure management systems
8 evaluated in this study.

9 Odor measurement methods using human olfactory senses are based on the use of
10 psychophysical theory. As the name implies, psychophysical methods are based on relationships
11 between psychological and physical attributes of sensory stimuli. The intensity of olfactory
12 stimuli reported by an individual is related to stimulus magnitude. For many odorants used in the
13 food and fragrance industry, there is a linear relationship between log olfactory intensity reported
14 by the individual and the air concentration of the odorant(s) present in air (Turk and Hyman,
15 1991). This relationship between perceived olfactory stimuli and intensity of sensation is
16 referred to as the fundamental psychophysical law (Stevens, 1957; Stevens, 1962). Data reported
17 in Figure 2C show that the total air concentration of VOCs correlate well to the log stimulus
18 intensity ($r^2 = 0.88$) and therefore, conforms to the fundamental psychophysical law. In
19 agreement with other olfactory studies, we observed that data quality was influenced by variables
20 associated with the subjective nature of intensity scales, fatigue, sex, age, race, and visual cues
21 (Cain et al., 1998; Degel and Koster, 1998; Liden et al., 1998; Livermore and Laing, 1998; Turk
22 and Hyman, 1991). However, the use of the defined odor standard Z-2 was found to reduce most
23 of the sampling variability associated with intensity scales. Evidence for this conclusion was
24 provided by the low average standard deviation reported by panelists for site evaluations (avg.
25 std. dev. = 0.14 odor units). A prerequisite that underlies all olfactory methods is the ability to
26 define and properly sample chemical odorants that constitute a particular odor. Accomplishing
27 this objective has been a formidable challenge, since it requires the use of both olfactory and
28 analytical methods to validate sampling methods. The results of this study demonstrate utility of
29 chemical methods in odor analysis and in the validation of air sample collection methods (i.e.,
30 Teflon bag sampling).

Emission Rate of Air Pollutants from Swine Manure Management Systems

Analysis of CH₄ emission rates, airborne VOC concentration, and odor intensity for the 29 swine manure management systems evaluated in this study indicated that manure management systems could be functionally classified according to the ratio of P to S concentrations. This analysis, however, provided limited insight into the differences in microbial processes associated with these systems. In an effort to further elucidate chemical and biological differences associated with the system classification, a detailed evaluation of effluent characteristics and gases (H₂S, NH₃, CH₄, VOCs) was conducted at four swine manure management systems that represented each of the four system classes. Each of the swine manure management systems chosen for the follow-up study were shown to exhibit the same relative profiles in CH₄ emission rate regardless of the flux measurement strategy employed (Table 1, chamber-based vs. Table 4, micrometeorological-based). These results provided additional support that manure management loading parameters influenced bioconversion efficiency. In systems with relatively low emission rates of CH₄ and NH₃ (Type 1 and 2 systems, Tables 3, 4, and 5), high concentrations of organic carbon and nitrogen (particulate C, H, N) were found to accumulate in the solution phase (Table 1). These systems were also observed to have the highest odor intensities. In contrast, Type 3 and 4 systems showed a lower tendency to accumulate effluent organic material (Fig. 3; Tables 1 and 3) and a much higher emission rate of CH₄ (Fig. 2; Table 1).

The emission rate of hydrogen sulfide (H₂S) appeared to be independent of the manure management system classification developed in this study (Table 5). This observation was unexpected since the emission rate of CH₄, NH₃, and VOCs were dependent upon the type of manure management system utilized (Fig. 2.; Table 5). Common precursors of H₂S in anaerobic swine manure management systems may include cysteine (cystine), methionine (indirect biotransformation), sulfur (S₀), thiosulfate (S₂O₃), or sulfate (SO₄). Sulfate (SO₄) is known to play a major role in mammalian physiology and is released (~0.1 to 1.4 g of SO₄ day⁻¹) in urinary excretions as SO₄-organic conjugates or SO₄ salts (Lehninger, 1988). Based on a daily SO₄ excretion rate of 0.13 g SO₄ pig⁻¹ day⁻¹ and a complete conversion to H₂S, a production facility with 4560 pigs (Site A, Table 5) is estimated to emit 593 g H₂S day⁻¹ through dissimilatory SO₄ reduction processes (Gottschalk, 1988; Postgate, 1984). This calculated value is similar to the

1 observed daily H₂S emission rate (Table 5, Site A), indicating that urinary SO₄ excretions may
2 account for a significant proportion of the sulfur (S)-precursors contributing to the H₂S emissions
3 measured in this study. The finding that SO₄ may be the major S-precursor contributing to H₂S
4 emissions provides microbiological insight into why H₂S emissions might be independent of
5 manure management system classification. All complex, organic forms of sulfur (S) require
6 energy expenditure to produce volatile, S-containing gases (i.e., formation of methyl mercaptan
7 or dimethyl disulfide from methionine; Gottschalk, 1988). Energy consuming microbial
8 processes have been shown to be highly sensitive to effluent environmental parameters such as
9 metal ion concentration and concentration of organic matter (Oleszkiewicz and Sharma, 1990;
10 Hill and Bolte, 1989). In contrast, SO₄ reduction is an energy-yielding process that is highly
11 favorable under environmental conditions observed in all manure management systems evaluated
12 in this study. These results suggest that future mass-balance studies should aim at
13 characterization of the S-cycle in swine manure management systems with special emphasis on
14 sources and fate of SO₄.

15 Manure management systems with high loading rates and relatively low CH₄-producing
16 activity showed up to a 26-fold increase in total VOC emissions when compared to low-odor
17 photosynthetic lagoons (Fig. 2 and Table 5). The data indicate that VOCs are more likely to be
18 of concern with systems employing high loading rates, while CH₄ and NH₃ are likely to be more
19 problematic with systems employing lower loading rates. In addition to nuisance concerns,
20 elevated VOC concentrations may present a concern to human health. A small number of
21 regulated industrial pollutants are present in airborne emission streams from swine production
22 facilities (Table 3). The air concentrations for these compounds at the source were found to be at
23 least one order of magnitude below exposure levels established for safe work environments by
24 occupational health organizations (Plog, 1988). However, the use of industrial exposure indices
25 may not be appropriate for assessing exposure to animal waste emissions due to the following
26 considerations: First, several agricultural waste pollutants are unique to agricultural systems and
27 thus, have no established exposure indices. Second, bioactive airborne pollutants, such as
28 microbial secondary metabolites, remain largely uncharacterized from swine production systems.
29 Bioactive compounds have been identified as a serious human health risk, since many of these
30 compounds have been shown to influence mammalian cell physiology in the part per billion and

1 sub-part per billion range (Andersson et al., 1998). Third, there is a lack of information on the
2 acute and chronic toxicological impacts of VOCs derived from swine manure on children and
3 individuals of compromised health. This concern is reflected in recent epidemiological studies
4 that have shown a higher incidence of psychological dysfunction and health-related problems in
5 individuals residing near large-scale swine production facilities (Thu et al., 1997; Schiffman et
6 al., 1995).

7 Ammonia emissions from the four intensively studied swine production systems were found
8 to violate release reporting requirements for NH_3 under the U.S. EPA Comprehensive
9 Environmental Response, Compensation, and Liability Act (CERCLA, U.S. EPA, 2000).
10 Emergency Planning and Community Right-to-Know Act (EPCRA) section 329(4), defines
11 facility to include stationary structures on a single site, or on contiguous or adjacent sites owned
12 or operated by the same person. Under this definition, the aggregated emission rate of registered
13 hazardous substances (i.e., NH_3 , H_2S , VOC, particulate matter) from all swine production facility
14 point sources is subject to release reporting requirements. The current reporting requirements for
15 NH_3 (and H_2S) are set at 100 pounds of $\text{NH}_3 \text{ day}^{-1}$ (CERCLA, U.S. EPA, 2000). The range for
16 NH_3 emissions from the four intensively studied swine production sites ranged from 101.7 kg
17 $\text{NH}_3 \text{ day}^{-1}$ (224 lbs. $\text{NH}_3 \text{ day}^{-1}$) to 369.2 kg $\text{NH}_3 \text{ day}^{-1}$ (813.9 lbs. $\text{NH}_3 \text{ day}^{-1}$). The observed
18 aggregate emission rates for swine production facilities evaluated in this study exceed the
19 CERCLA reporting requirements for NH_3 by 55% to 88%. Under section 304 of EPCRA, the
20 “owner or operator” of a facility is required to report immediately to the appropriate State
21 emergency response commissions and local emergency planning committees when there is a
22 release of a CERCLA hazardous substance. The results indicate that NH_3 emissions from swine
23 production facilities have the potential to exceed release reporting requirements enforced by the
24 U.S. EPA.

25 Lagoons with established anoxic bacterial photosynthetic populations (Type 4 systems;
26 bacteriochlorophyll *a* concentrations above 40 nmol/ml) showed lower odor intensities, lower air
27 concentrations of VOCs, and lower emission rates of VOCs when compared to other swine
28 manure management systems (Fig. 3; Tables 3 and 4). Photosynthetic bacteria carry out the
29 process of photosynthesis under anaerobic conditions. These requirements for photosynthesis
30 differ greatly from algae and plant species that use water as an electron source for photosystem II

1 and evolve oxygen in this reaction (Kobayashi and Kobayashi, 1995). Instead of utilizing water
2 as a reductant, anoxic photosynthesis is dependent on substrates such as H₂S, hydrogen (H₂), and
3 VOCs to provide reducing equivalents, while light from the sun provides the energy source
4 (Gottschalk, 1988). Bacteria capable of anoxic photosynthesis are categorized into one of four
5 major groups (purple sulfur, purple non-sulfur, green sulfur, and green-gliding) based on the
6 presence of specific types of bacteriochlorophyll, phylogenetic characteristics, and metabolic
7 capabilities (Gottschalk, 1988; Siefert et al., 1978). All four groups of photosynthetic bacteria
8 are able to utilize organic substrates (VOCs) as a source of carbon and the green-gliding and
9 purple bacteria are able to use organic substrates as proton donors. However, a novel species of
10 *Rhodobacter* (*Rhodobacter* sp. PS9) dominates the photosynthetic population (~20% of the total
11 microbial community structure) in all photosynthetic swine lagoon systems examined in this
12 study (Do et al., 1998; Do et al., 1999). The physiological characteristics of this purple non-
13 sulfur photosynthetic bacterium provides evidence for the observed degradation of VOCs and
14 decreased odor emissions from photosynthetic swine waste lagoons.

16 CONCLUSIONS

17 The lack of knowledge concerning functional aspects of swine manure management systems
18 has complicated present efforts to develop or improve emission abatement technologies to meet
19 the stringent air quality and nuisance regulations presently imposed by several States. The task
20 of elucidating functional aspects of swine manure management systems is often convoluted by
21 the plethora of manure management strategies presently used in the swine industry. In the
22 absence of appropriate compatibility or functional measures, emission abatement strategies are
23 often paired with swine manure management systems based only on empirical observations. As
24 a result, the performance of these abatement methods is difficult to predict and often impossible
25 to improve through scientific methods. Effluent concentrations of P and S are shown in this
26 study to be a useful tool in the classification of swine manure management systems according to
27 functional aspects of the system. The methods described in this study provide an inexpensive
28 means to rapidly assess best management practices for swine manure management systems and
29 also provide a means by which to identify swine production systems that represent a potential air
30 quality or nuisance concern.

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TABLE 1. Physical properties, elemental composition, and CH₄ emission rates determined by flux chamber methods for 29 swine manure management systems located in Iowa, Oklahoma, and North Carolina during the months of August and September, 1997. Values represent the mean \pm the standard error of the mean.

Parameter †	Site Classification ‡			
	Type 1 ‡	Type 2	Type 3	Type 4
Site number (n)	n = 6	n = 7	n = 6	n = 10
Manure management system description	DP; n = 5 PP; n = 1	EB; n = 3 CLB; n = 3 ST; n = 1	L; n = 6	PL; n = 10
Methane emission rate (g CH ₄ system ⁻¹ hr ⁻¹)	636 \pm 47	1830 \pm 148	13900 \pm 760	11990 \pm 540
Volatile solids loading rate (kg VS day ⁻¹ m ⁻³)	79 \pm 3.0	35 \pm 2.6	0.3 \pm 0.05	0.07 \pm 0.02
pH	7.1 \pm 0.04	7.3 \pm 0.06	7.3 \pm 0.06	7.1 \pm 0.03
Solid content (mg/ml)	21.9 \pm 0.9	13.4 \pm 0.6	3.8 \pm 0.4	2.8 \pm 0.1
% Carbon (% dry mass)	37.2 \pm 0.6	33.7 \pm 0.5	16.6 \pm 0.3	14.1 \pm 0.3
% Hydrogen (% dry mass)	5.2 \pm 0.3	4.9 \pm 0.2	2.3 \pm 0.2	1.8 \pm 0.1
% Nitrogen (% dry mass)	3.0 \pm 0.2	2.9 \pm 0.2	1.8 \pm 0.2	1.5 \pm 0.1
Ca (mg/L)	301 \pm 38	173 \pm 24	58 \pm 5	119 \pm 10
Cu (mg/L)	18 \pm 6.2	1.7 \pm 0.2	0.2 \pm 0.1	0.2 \pm 0
Fe (mg/L)	47 \pm 21.5	8.9 \pm 1.2	1.2 \pm 0.2	0.7 \pm 0.4
K (mg/L)	1380 \pm 400	1040 \pm 134	624 \pm 18	0.9 \pm 0.3
Mg (mg/L)	128 \pm 19	62 \pm 10	20 \pm 1.6	39 \pm 4.0
Mn (mg/L)	3.2 \pm 0.8	0.9 \pm 0.2	0.1 \pm 0	0.3 \pm 0.2
Na (mg/L)	241 \pm 86	225 \pm 20.8	165 \pm 4.6	18 \pm 6.3
P (mg/L)	504 \pm 26	153 \pm 12.1	65 \pm 4.5	0.2 \pm 0
S (mg/L)	108 \pm 8	39 \pm 5.3	15 \pm 0.4	8 \pm 1.8
Zn (mg/L)	18.7 \pm 8	2.7 \pm 0.4	0.4 \pm 0.1	0.1 \pm 0

† Values represent the mean for samples listed in Fig. 1. Instrumental error was < 1% for CHN analysis and < 0.1% for ICP-AES analysis.

‡ Manure storage system designation as defined in Fig. 1. Type 1 systems represent confinement buildings with short and long term, under-slat storage (pull-plug and deep-pit systems). Type 2 systems represent earthen, concrete, or steel-lined manure storage basins. Type 3 and Type 4 systems represent lagoon systems without and with anoxic photosynthetic blooms, respectively. Subclassification designations: PL = phototrophic lagoon; L = lagoon; EB = earthen basin; CLB = concrete-lined basin (outdoor); ST = steel tank (outdoor); DP = deep pit; PP = pull-plug.

TABLE 2. Results for the pairwise comparison of element concentrations present in effluent samples from 29 swine manure management systems. Values indicate the nonparametric measure of association between pairwise comparisons of elements.

Element	Nonparametric measure of association (Spearman's rho value)									
	Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Zn
Ca	1	0.65	0.80	0.92	0.82	0.37	0.66	0.66	0.66	0.66
Cu		1	0.92	0.70	0.66	0.83	0.65	0.96	0.92	0.96
Fe			1	0.64	0.78	0.95	0.59	0.93	0.89	0.91
K				1	0.36	0.56	0.96	0.74	0.74	0.67
Mg					1	0.83	0.30	0.69	0.68	0.66
Mn						1	0.50	0.87	0.85	0.84
Na							1	0.67	0.66	0.62
P								1	0.94	0.96
S									1	0.93
Zn										1

TABLE 3. The mean concentration of trace gases and VOCs present in air samples from four swine manure management systems representing each system class. Values reported represent the sample mean for a 24 hr sampling period and the standard error was less than 3% of the mean. Sample number site⁻¹: VOC, n = 12; NH₃, CH₄, and H₂S, n = 24.

Peak # and Retention time (min.)	Compound	Swine manure management system type (Analyte air concentration ($\mu\text{g m}^{-3}$) and Percent total peak area (%))			
		Type 1 †	Type 2	Type 3	Type 4
Spec	Ammonia	9623	7923	9362	10843
GC-FID	Methane	5002	8406	18703	24406
GC-FPD	Hydrogen Sulfide ‡	54	48	27	29
1 (4.8)	Dimethyl disulfide	12 (1.3)	nd	17 (6.8)	nd
2 (6.1)	2-Butanol	8 (0.8)	nd	19 (7.5)	nd
3 (7.5)	Dimethyl trisulfide	nd	nd	13 (5.2)	nd
4 (8.6)	Unknown	nd	nd	- (2.9)	nd
5 (10.6)	Acetic acid	281 (15.2)	262 (7.6)	11 (2.7)	2 (2.3)
6 (11.9)	Propionic acid	126 (11.1)	50 (2.3)	5 (1.9)	4 (8.2)
7 (12.4)	Isobutyric acid	23 (2.5)	107 (11.4)	6 (2.2)	nd
8 (13.3)	Butyric acid	142 (15)	586 (32)	13 (5.1)	5 (12.9)
9 (14.0)	Isovaleric acid	73 (8.3)	98 (6)	3 (1.2)	nd
10 (15.0)	n-Valeric acid	43 (4.9)	360 (27)	5 (2.0)	1 (0.7)
11 (15.7)	Isocaproic acid	nd	10 (0.5)	nd	nd
12 (16.0)	n-Caproic acid	nd	105 (7.4)	nd	nd
13 (16.1)	Unknown	- (1.2)	nd	nd	nd
14 (16.6)	Heptanoic acid	nd	8 (0.3)	nd	nd
15 (17.2)	Benzyl alcohol	nd	nd	2 (1.2)	nd
16 (18.8)	Phenol	9 (1.5)	24 (1.6)	8 (6.9)	3 (9.9)
17 (19.7)	4-Methyl phenol ‡	85 (19.6)	32 (2.7)	9 (7.5)	3 (17.8)
18 (20.9)	4-Ethyl phenol ‡	3 (0.7)	2 (0.2)	4 (3.3)	1 (6)
19 (21.9)	2-Amino acetophenone ‡	nd	nd	nd	0.2 (0.4)
20 (23.4)	Indole	nd	1.1 (0.2)	0.8 (0.6)	0.1 (0.5)
21 (23.7)	Hexadecanoic acid	nd	nd	9 (7.8)	5 (33)
22 (24.2)	3-Methyl indole	0.5 (0.2)	1.4 (0.3)	1.3 (1.1)	0.2 (0.7)
Total concentration of non-methane VOCs identified in air ($\mu\text{g m}^{-3}$)		806	1647	126	25
Percent of total peak area (%)		82.3	99.5	65.9	92.4

† Micrometeorologically-defined sampling parameters: Type 1 = mechanically-ventilated exhaust flow rate = 110,000 m³ hr⁻¹, sampling position at the fan orifice; Type 2 = 39 m diameter basin, z=ZINST(0.1 cm roughness length, 1950 cm radius = 70 cm sampling height); Type 3 = 92 m diameter lagoon, z=ZINST(0.1 cm roughness length, 4600 cm radius = 189 cm

1 sampling height); Type 4 = a primary 100 m diameter photosynthetic lagoon, $z=ZINST(0.1$ cm
2 roughness length, 5000 cm radius = 191 cm sampling height).
3 ‡ U.S. EPA priority pollutants identified in air samples: cresols (isomers and mixtures), H_2S ,
4 phenol, and acetophenones. nd = analyte not detected.
5

TABLE 4. Mean horizontal flux rate and mean emission rate for analytes collected over a 24 hr sampling period from swine manure management systems sampled in Table 3 and described in Table 5. Gas flux rates were measured using the Theoretical Profile Shape micrometeorological method.

Parameter	Swine manure management system type			
	Type 1	Type 2	Type 3	Type 4
Mean wind velocity ^a (cm s ⁻¹) or ventilation rate ^b (m ³ hr ⁻¹) during sampling period	110,000 ^b	190 ^a	128 ^a	90 ^a
Ammonia flux rate (ng NH ₃ cm ⁻² s ⁻¹)	66 †	167	109	89
Ammonia emission rate (g NH ₃ system ⁻¹ hr ⁻¹)	1060	1900	7700	6270
Methane flux rate (ng CH ₄ cm ⁻² s ⁻¹)	34 †	178	218	200
Methane emission rate (g CH ₄ system ⁻¹ hr ⁻¹)	550	2010	15410	14120
Hydrogen sulfide flux rate (ng H ₂ S cm ⁻² s ⁻¹)	0.37 †	1.10	0.32	0.24
Hydrogen sulfide emission rate (g H ₂ S system ⁻¹ hr ⁻¹)	5.9	12.5	22.7	16.9
Priority pollutant (PP) flux rate (ng PP cm ⁻² s ⁻¹) ‡	1.04 †	2.30	0.56	0.30
Priority pollutant emission rate (g PP system ⁻¹ hr ⁻¹) ‡	16.6	26.1	39.6	20.9
VOC flux rate (ng VOC cm ⁻² s ⁻¹)	5.60 †	35.0	1.60	0.21
VOC emission rate (g VOC system ⁻¹ hr ⁻¹)	89.9	394.0	113.1	14.5
Total air pollutant emission rate (g TAP system ⁻¹ hr ⁻¹)	1720	2420	15550	14150

† System flux rate calculated using an active surface area of 4,459,000 cm² and assumes a homogenous emitting source for active surfaces.

‡ U.S.-EPA priority pollutants identified in air samples: cresols (isomers and mixtures), hydrogen sulfide, phenol, and acetophenones.

TABLE 5. Emission rates for air pollutants collected over a 24 hr sampling period from swine manure management systems sampled in Tables 3 and 4. Values were calculated from flux measurements that employed the Theoretical Profile Shape micrometeorological method.

Parameter	Swine manure management system type			
	Type 1 ‡	Type 2	Type 3	Type 4
Annual production number and type	Feeder to finish 13680 animals yr ⁻¹	Farrow to finish 8200 animals yr ⁻¹	Feeder to finish 14170 animals yr ⁻¹	Farrow to feeder 18500 animals yr ⁻¹
Site manure management system description †	4 - DP	2 - CLB 2 - PP	1 - L PFS ‡	2 - PL PFS ‡
Ammonia emission (kg NH ₃ site ⁻¹ day ⁻¹)	101.7	141.7	232.8	369.2
Methane emission (kg CH ₄ site ⁻¹ day ⁻¹)	52.8	122.7	466.1	831.0
Hydrogen sulfide emission (kg H ₂ S site ⁻¹ day ⁻¹)	0.6	0.9	0.7	1.0
Priority pollutant (PP) emission (kg PP site ⁻¹ day ⁻¹)	1.6	2.1	1.2	1.2
VOC emission (kg VOC site ⁻¹ day ⁻¹)	8.6	23.2	3.4	0.9
Combined air pollutant emission (kg TAP site ⁻¹ day ⁻¹)	165	291	704	1203

† Manure storage system description: PL = phototrophic lagoon; PFS = continuous pit flush system; L = lagoon; EB = earthen basin; CLB = concrete-lined basin (outdoor); DP = deep pit; PP = pull-plug.

‡ The emission rate for analytes released from the continuous pit flush systems was calculated based the flux rates (Table 4) and the total pit surface area actively flushed with recycled lagoon liquid. The active surface area for PFS systems at site 3 and 4 was 510 m² and 890 m², respectively.

FIGURE 1. Flux rate of CH₄ from swine manure management systems differing in volatile solids loading rate as determined by the Theoretical Profile Shape micrometeorological method and using the tunable diode laser method. The (A) CH₄ flux over a 30 hr period from a swine manure lagoon (0.12 kg volatile solids day⁻¹ m⁻³) and over a 25 hr period for a swine manure basin (37 kg volatile solids day⁻¹ m⁻³). The time period between CH₄ measurements for sites was approximately 16 hours and is indicated by the broken X-axis. Oneway Anova (B) (t-test) for CH₄ flux data and the Tukey-Kramer HSD means comparison table showing the absolute difference in the means minus the least significant difference (Alpha level = 0.05).

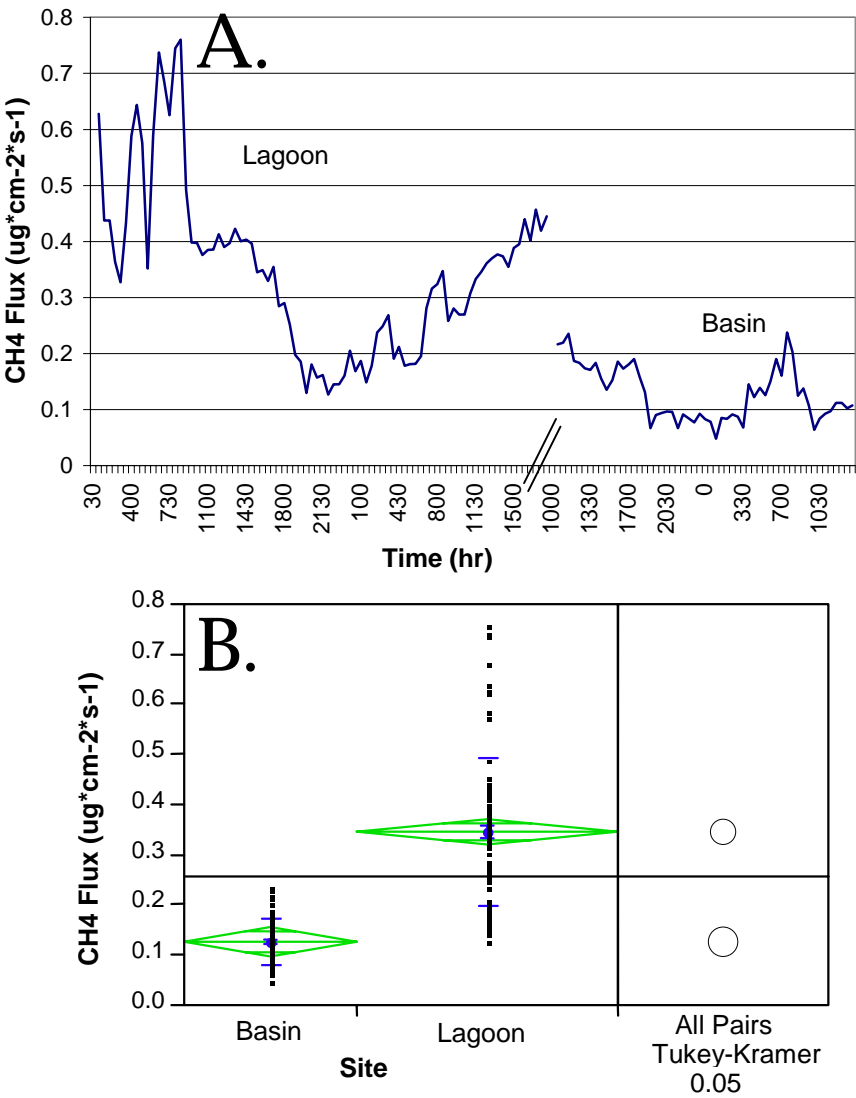
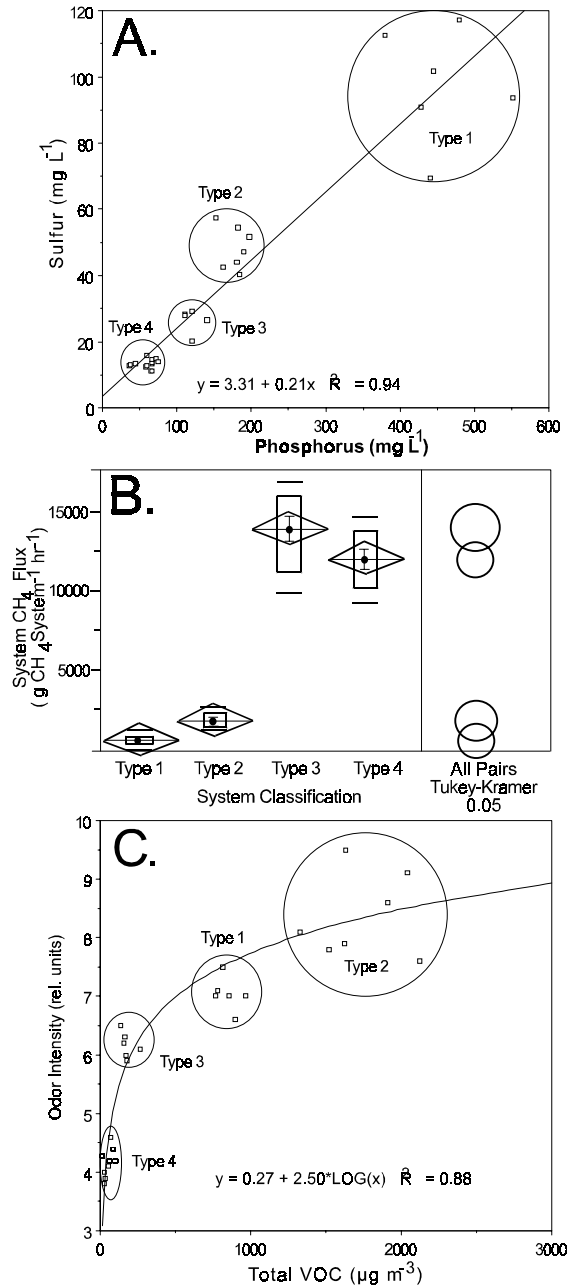


FIGURE 2. Cluster analysis for the (A) concentration of total phosphorous versus total sulfur in effluent from 29 swine manure management systems. The (B) Anova (compare all pairs) for CH₄ emission rate from swine manure management systems categorized according to phosphorus and sulfur concentrations and the Tukey-Kramer HSD means comparison table (Alpha level = 0.05). The (C) correlation between the concentration of VOCs present in air from manure management systems versus the mean odor intensity.



1 **FIGURE 3.** Gas chromatograms of volatile organic emissions from swine manure storage
2 systems representing the four system subtypes. From top to bottom: Air sample collected in a
3 deep pit (Type 1), air sample collected over a concrete-lined basin (Type 2), air sample collected
4 over a lagoon (Type 3), and air sample collected over a photosynthetic lagoon (Type 4). Peak
5 reference numbers correspond to organic compounds listed in Table 3.

